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**AQUEOUS EMULSION OF CROSS-LINKED TER-POLYMERS FREE OF MICROGEL AND METHOD OF MAKING SAME****Robert McLellan Fitch, Cynwyd, Pa., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware****No Drawing. Filed Apr. 8, 1960, Ser. No. 20,802****17 Claims. (Cl. 260—29.7)**

This invention relates to novel aqueous dispersion polymer compositions derived from monomer compositions essentially comprising at least one monoethylenically unsaturated monomer having a terminal vinylidene group  $>C=CH_2$  and to the technique of polymerizing such monomers to aqueous dispersion polymer compositions having a high polymer content. More particularly, the invention relates to aqueous dispersion copolymer compositions derived from monomer mixtures containing a plurality of monoethylenically unsaturated monomers having the terminal vinylidene group and including an ester of an alpha ethylenically unsaturated monocarboxylic acid with an alkanol and to the process of copolymerizing such monomer mixtures by aqueous emulsion polymerization in the presence of an effective small proportion of a copolymerizable difunctional chain extender having two terminal vinylidene groups per molecule.

Aqueous emulsion polymerization of mixtures of ethylenically unsaturated monomers, at least ternary in composition, are described in United States Patents 2,787,603, 2,787,561, 2,753,318, 2,868,752 and 2,918,391. Examples in these several patents show aqueous polymerization charges in which the non-polymerizable components constitute a preponderant proportion of the total composition, the copolymer content of the product ordinarily being no greater than 45% by weight and in most instances less than 40%. While products having this copolymer content can be prepared in adequately stable aqueous dispersion form and find practical utility at these concentrations, it is desirable to have dispersion products in which the content of the copolymer is significantly higher than that of the typical compositions described in these patents. Two significant advantages of stable high solids content aqueous dispersion copolymer compositions are the economic advantage of (1) transporting less water and more copolymer per unit of aqueous product shipped and (2) the application of greater solids content per coat with the accompanying lesser amount of water to be removed by volatilization in drying the coating.

Although aqueous dispersion copolymer products having a moderately higher content of copolymer can be obtained by following the respective examples in the aforementioned patents using an increased proportion of monomer charge and a correspondingly decreased proportion of water, the polymerization conditions are changed sufficiently to result in the characteristics of the copolymer being different from those of the copolymer prepared at the usual lower concentration. Ordinarily, undesirable proportions of coagulum result in such processing at the higher concentrations. While changes in the polymerization process can be effected to provide a substantially equivalent copolymer in aqueous dispersion form, the economic advantage of high solids content of copolymer is offset by economic disadvantages in the altered process. It is known that high solids content is obtained by increasing the stability of the aqueous dispersion of the polymer during and after polymerization. Increased stability is accomplished by increasing the particle-size and by continuous addition of monomer during the polymerization. However, these changes have the effect

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of reducing the molecular weight of the polymer and of increasing the polymerization time. The polymerization time can be reduced by increasing the proportion of polymerization initiator, but this also results in reduced molecular weight of the polymer.

I have discovered that stable aqueous dispersion polymer compositions having a high content of polymer are prepared economically by conducting the aqueous emulsion polymerization of one or more polymerizable monovinylidene unsaturated monomers in the presence of an effective small proportion of a difunctional polymer chain extender which promotes an adequate increase in molecular weight. Suitable chain extenders have two terminal vinylidene groups and effective proportions ordinarily range from  $10^{-5}$  to 1 mol percent based on the total mols of polymerizable monomers. The maximum proportion of the bis-vinylidene chain extender in any particular combination of monomers is that which when exceeded results in formation of microgel. This maximum proportion is readily determined by pilot experimentation at several levels of bis-vinylidene chain extender concentration in the range of up to 1 mol percent of the total monomer content. The respective relative viscosities of the several resulting pilot polymers are determined and the values plotted against the concentration of the difunctional chain extender. The curve representing the plotted results ordinarily will show an inflection corresponding to a maximum relative viscosity under the particular polymerization conditions selected. The concentration of difunctional chain extender corresponding to this inflection in the curve is the maximum useful concentration under the particular polymerization conditions. Use of a concentration of the difunctional chain extender beyond this maximum results in microgel formation which is reflected by a decrease in the relative viscosity of the polymer.

The following are typical pilot experiments to illustrate determination of the maximum useful concentration of the difunctional chain extender in a simple monomer composition.

**SERIES A**

A polymerization charge of 100 grams of methyl methacrylate, 130 grams of distilled water, 10 ml. of an aqueous solution of ammonium persulfate,  $(NH_4)_2S_2O_8$ , at 5% concentration and 10 ml. of an aqueous solution of sodium lauryl sulfate, "Duponol" C, at 5% concentration are charged into a sealable bottle, capped and tumbled for one hour at  $85^\circ C$ . Additional polymerization charges are prepared by replacing an aliquot portion of the methyl methacrylate monomer with a mixture of vinyl methacrylate and methyl methacrylate having a content of 0.112% of the vinyl methacrylate. The respective proportions of the monomer mixture supplied is sufficient to provide  $10^{-3}$ ,  $10^{-2}$ ,  $10^{-1}$  and 1 mol percent of the bis-vinylidene chain extender, i.e., vinyl methacrylate, based on the mols of methyl methacrylate. These polymerization charges are processed the same as the methyl methacrylate charge containing no bis-vinylidene chain extender. The relative viscosity of the resulting aqueous polymerization products is determined at 0.5% polymer content in dimethyl formamide. The following table is typical of the relative viscosity data.

Table 1

Mol percent vinyl methacrylate:	Relative viscosity
0	1.29
$10^{-3}$	1.30
$10^{-2}$	1.31
$10^{-1}$	1.52
1	1.08